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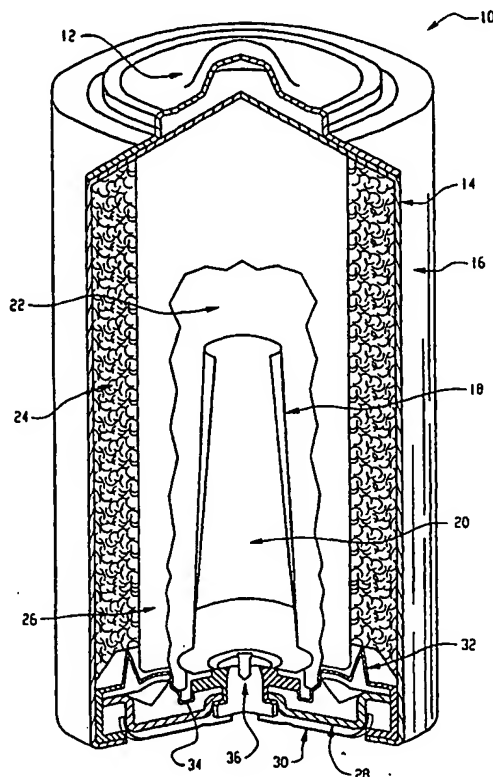
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(54) Title: IMPACT MODIFIED POLYSTYRENE SEALS FOR ELECTROCHEMICAL CELLS

(57) Abstract

A sealing member for an electrochemical cell is formed of a high impact modified styrenic polymer blend which may include a styrenic polymer and an impact modifying agent which increases the toughness of the styrenic polymer. The styrenic polymer based sealing member has several advantages over conventional cell seals and sealing gaskets, including lower cost, better processability and improved chemical resistance to alkaline medium. Also provided are galvanic cells including the seal member, in particular miniature alkaline air cells including the seal member as a gasket.



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IMPACT MODIFIED POLYSTYRENE SEALS FOR ELECTROCHEMICAL CELLS

5 This invention relates to improved sealing members for electrochemical cells, such as seals for alkaline galvanic cells and sealing gaskets for miniature cells, and particularly to non-ventable gaskets for miniature air cells.

10 Electrochemical cells, such as miniature alkaline air cells, are stable, high-energy sources for electrical devices, such as hearing aids. An alkaline electrolyte must be sealed within the confines of the cell to prevent corrosive damage to the exterior of the cell and possibly to the electrical device in which it is housed.

15 In the case of a miniature air cell, a continuous supply of air must be provided to the surface of the air electrode. Generally, a miniature alkaline air cell comprises an outer metal container having at least one air opening in its base to provide air to the active air electrode, a hydrophobic film layer, an air electrode, a separator layer, an anode mask, and an electrolyte. The cell assembly is capped with a gasket and metal cell cover which seals the open end of the cell container thereby sealing in the alkaline
20 electrolyte. The term "gasket" as used herein refers to a non-ventable sealing member for providing a fluid-tight joint between battery components.

25 Seals for galvanic cells, including gaskets for alkaline air cells, have generally been made from nylon, polypropylene or polysulphone, with nylon being preferred, especially nylon 66. However, nylon seals for alkaline galvanic cells, including nylon gaskets for miniature alkaline air cells, have major disadvantages.

30 First, nylon absorbs moisture making it susceptible to hydrolytic degradation in a corrosive electrolyte. As a result of the tendency for nylon to absorb moisture, it must be dried prior to moulding. After moulding, the dimensions and properties of the resulting

seal or gasket are affected by the tendency of nylon to absorb moisture. Hydrolytic degradation of nylon occurs through chain scission of amide bonds. Chain scission embrittles the material, leading to seal failure and leakage of the cell. Thus, in the case of a nylon gasket, embrittlement makes the gasket susceptible to stress cracking which
5 leads to gasket failure and leakage of electrolyte from the cell.

To overcome this in alkaline galvanic cells, protective coatings are sometimes used on the internal side of the seal. In particular, nylon seals for alkaline galvanic cells are generally provided with an asphaltic coating. Application of the asphaltic coating
10 involves additional steps and materials which increase the overall cost of the seal.

Another problem with nylon seals for alkaline galvanic cells is that they have a relatively high ultimate elongation. For safety reasons, seals for alkaline galvanic cells are designed to provide controlled release of pressure in the event that the internal
15 pressure of the galvanic cell increases beyond an acceptable limit. This is achieved by forming the seal with a relatively thin portion which is designed to rupture if the internal pressure of the galvanic cell increases beyond an acceptable limit. Sufficient space must be provided within the cell to allow the thin portion to extend and rupture. Under normal moisture conditions, nylon extends over 300% of its initial length. This high
20 level of elongation requires large amounts of internal cell space which limits the seal and cell design. Accordingly, it would be desirable to utilise a material for seal construction which meets the necessary physical and chemical requirements for use as a seal material in an alkaline cell, and which has a relatively lower ultimate elongation.

25 Another disadvantage with nylon galvanic cell seals is that the physical properties of the seal are dependent upon the moisture content of the nylon. In particular, the strength of nylon is dependent upon its moisture content, which in turn is dependent upon relative humidity. Accordingly, the vent pressure, i.e. the pressure at which the thin portion of the seal ruptures, of nylon galvanic cell seals is undesirably
30 dependent on relative humidity.

Galvanic cell seals made of polypropylene are subject to extensive softening at the high end of possible use temperatures, i.e. 75-85°C. This softening results in lower deflection temperatures under load and excessive stress relaxation in the compressive sealing zones of the seal and hence leakage of electrolyte and unreliable cell performance.

The use of polysulphone as a material for making galvanic cell seals has been relatively limited on account of its relatively high cost (approximately 2.5 times the cost of nylon 66). In addition to its relatively high cost, polysulphone also has a tendency to absorb moisture, and must be dried to a moisture content of less than or about 0.02% before it can be moulded into a seal. This extra step of drying polysulphone before it can be moulded further increases the overall cost of forming a galvanic cell seal from polysulphone.

We have now found, surprisingly, that galvanic cell seals having improved performance characteristics and other advantages, as compared with known seals, can be provided, if made or comprised of an impact modified styrenic polymer. In particular, as compared with conventional seals, especially nylon, seals made of impact modified styrenic polymer exhibit excellent chemical resistance to alkaline medium. absorb very little water, have a low coefficient of linear thermal expansion. exhibit good heat resistance properties at higher pressures. cool quickly after moulding. have a low melt viscosity. have relatively low tensile strength. have high impact toughness. have a relatively high glass transition temperature, have a relatively low elongation to break, and higher hydrogen permeability. These properties result in a galvanic cell seal which can be manufactured at a much lower cost, and which exhibits excellent performance characteristics which do not vary significantly over the range of temperatures and relative humidity encountered during cell use.

We have also found that a gasket for a miniature alkaline air cell can be provided that is less sensitive to moisture and hydrolytic degradation, by forming the gasket of a styrenic polymer blend. As a result, the use in a miniature alkaline air cell of a gasket

which is formed of a styrenic polymer blend can provide a miniature alkaline air cell which is substantially less likely to exhibit electrolyte leakage on account of gasket failure.

5 Accordingly, in a first aspect, the present invention provides a galvanic cell sealing member formed of a high impact styrenic polymer blend. More particularly, the styrenic polymer blend may comprise a blend a styrenic polymer and an impact modifying agent, or may be formed of a blend of high impact polystyrene and polybutadiene rubber to form a styrenic phase and discrete rubbery phase. In one
10 embodiment, the sealing member is a gasket for a miniature cell, in particular a miniature alkaline air cell.

 In a second aspect, the present invention provides a galvanic cell including a sealing member as defined above. In one embodiment, the cell is a miniature alkaline
15 air cell and the sealing member is a gasket for the miniature alkaline air cell.

 In a preferred embodiment of the second aspect, a miniature air cell is provided comprising:

 a container having a base, an upright sidewall and an open-ended top, and having
20 at least one air opening in the base;

 a cell assembly housed in the container having an air electrode in electrical contact with the container, an anode material situated above the air electrode, a separator layer between the air electrode and the anode material, and an electrolyte in ionic contact with the air electrode and the anode material;

25 a cell cover in electrical contact with said anode material; and
 an electrically insulating gasket interposed and compressed between the cell container and cover, the gasket formed of a styrenic polymer blend.

 Preferably, the styrenic polymer blend includes an anti-stress relaxation agent, preferably poly(phenylene oxide) or an inorganic filler.

The present invention will be further understood by reference to the drawings, in which:

Figure 1 is a perspective view of a typical cylindrical alkaline cell with portions broken away to show the construction thereof;

5 Figure 2 is a graph showing a comparison of the percentage weight loss for a nylon tensile bar floated on a 37% potassium hydroxide solution in a fluoropolymer vial and placed in an oven at 130°C, and for a general purpose polystyrene tensile bar subjected to the same conditions;

10 Figure 3 is a comparison of percent weight loss for a nylon microtensile bar having a 0.23 mm (0.009 inch) thick section submerged in 37% potassium hydroxide solution in a sealed fluoropolymer bottle and placed in an oven at 95°C, and for a variety of different polystyrene based microtensile bars of identical size and shape which are subjected to identical conditions as the nylon microtensile bar;

15 Figure 4 is an attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrograph of the surface of an untreated sample of general purpose polystyrene compared with the spectrograph of the surface of a general purpose polystyrene sample which was treated by exposure to a 37% potassium hydroxide solution at 130°C for 39 days;

20 Figure 5 is an ATR-FTIR spectrograph of the surface of an untreated nylon sample, compared with the surface of a nylon sample treated with exposure to a 37% potassium hydroxide solution at 130°C for 39 days;

Figure 6 is a graph of stress relaxation verses time at room temperature for Noryl® EM6100, HIPS and Zytel® 101F;

25 Figure 7 is a graph of rate of stress relaxation verses time for Noryl® EM6100, HIPS and Zytel® 101F;

Figure 8 is a sectional side elevation view taken through an assembled miniature alkaline air cell; and

Figure 9 is a partial cross-sectional side view of the assembly of Figure 8.

30 Shown in Figure 1 is a typical cylindrical alkaline galvanic cell or battery 10. Battery 10 includes a plated steel positive cover 12, a steel can 14, a metallised plastic

film label 16, powdered zinc anode 18, brass current collector 20, potassium hydroxide electrolyte 22, a manganese dioxide and carbon cathode 24, a non-woven fabric separator 26, a steel inner cell cover 28, and a plated steel negative cover 30. Interposed between the alkaline potassium hydroxide electrolyte 22 and steel inner cell cover 28 is
5 a seal 32.

Seal 32 performs four important functions. First, it serves as an electrical insulator which electrically isolates steel can 14 from the anode. Second, seal 32 prevents electrolytes from leaking from the battery. Third, seal 32 includes a relatively
10 thin area 34 which is designed to rupture in the event that the internal pressure of the battery exceeds a predetermined limit. Fourth, seal 32 regulates the rate of hydrogen gas egress from the battery cell.

Referring to Figures 8 and 9, there is shown a sectional side elevation of a
15 miniature alkaline air cell 10. The internal cell components comprise an air electrode 17, which is a laminated electrode that has a first layer 16 which may comprise a mixture of active materials such as activated carbon and binder, a second layer 18 which is a current collector, and a third layer 12 which is a hydrophobic membrane. The internal components also comprise an anode mask 13, and a separator layer 14 between
20 the air electrode and the anode mask. Separator layer 14 permits passage of electrolyte ions but prevents migration of ions in the air electrode to the anode mask. The internal cell components 10, 12, 13, 14, 16, 17 and 18 are housed in container 21 which is in intimate electrical contact with the current collector 18 and sealed at its open end by an electrically insulating sealing gasket 22 and cell cover 23 which is in electrical contact
25 with anode 3. Sealing gasket 22 is radially squeezed between cell container 21 and cover 23 so as to form a primary barrier to electrolyte leakage. The base of container 21 includes at least one air opening 30 which provides ingress and egress of air within air diffusion chamber 34 to air electrode 17. The container base may be separated from the air electrode by a thin resiliently deformable ring 35.

Sealing gasket 22 may be formed, such as by injection moulding, and inserted between container 21 and cell cover 23 during assembly of cell 10. Alternatively, sealing gasket 22 can be formed by insert moulding sealing gasket 22 onto container 21 or onto cover 23.

5

While the embodiment of the invention illustrated in Figures 8 and 9 is a miniature air cell, it is to be understood that the invention applies to electrochemical cells generally, including alkaline cells such as AA, AAA, AAAA, C and D cells.

10

The sealing member, as for example illustrated in Figure 1 by seal 32 or in Figures 8 and 9 by sealing gasket 22, is made from, or comprised of, an impact modified polystyrene material. Preferred modified polystyrene materials may be comprised of a styrenic polymer blended with an impact modifier which reduces the brittleness of the styrene and increases its toughness.

15

Examples of suitable styrenic polymers include general purpose polystyrene (GPPS) and syndiotactic polystyrene (SPS). General purpose polystyrene is an amorphous, widely used commodity polymer which is extremely brittle at galvanic cell use temperature, due to its glass transition temperature of 100°C. Syndiotactic polystyrene, which is sold under the trade name Qestra[®] by Dow Chemical Company, is a semi-crystalline thermoplastic polymer. However, as opposed to the unordered atactic configuration of amorphous general purpose polystyrene, syndiotactic polystyrene is comprised of styrene monomer units arranged in a highly ordered alternating configuration along the polymer chain. This ordered structure allows the polymer chains to crystallise. The crystallinity improves the strength and heat resistance of the material near and above the glass transition temperature. Accordingly, on account of the improved heat resistance and strength properties, syndiotactic polystyrene is preferred. Other styrenic polymers which may be suitable for preparing the galvanic cell sealing members of the invention include styrenic copolymers and halogenated styrenic polymers.

30

Examples of suitable impact modifiers for reducing the brittleness and increasing the toughness of styrenic polymers include polyolefinic thermoplastic elastomers and tri-block copolymers with an elastomeric block between two rigid thermoplastic blocks. Examples of polyolefinic thermoplastic elastomers include those
5 polymerised from ethylene, octane, and butylene monomer units which are copolymerised, such as in the presence of a metallocene catalyst, to produce saturated hydrocarbon rubbery materials. Preferred tri-block copolymer impact modifiers which may be used for preparing impact modified styrenic polymer blends from which galvanic cell sealing members may be prepared include those having thermoplastic
10 blocks which are amorphous polystyrene. The amorphous polystyrene blocks provide improved miscibility in styrenic polymers such as SPS and GPPS as compared with polyolefinic elastomers. Preferred tri-block copolymer impact modifiers include styrene-butadiene-styrene (S-B-S), styrene-isoprene-styrene (S-I-S), styrene-ethylene/butylene-styrene (S-EB-S) and styrene-ethylene/propylene-styrene (S-EP-S)
15 block copolymers. S-EB-S and S-EP-S copolymers are more preferred because they do not contain any sites of unsaturation, and are therefore less susceptible to oxidative degradation.

Another suitable impact modified styrenic polymer which can be used in the
20 practice of this invention is high impact polystyrene (HIPS). High impact polystyrene is produced by dissolving polybutadiene rubber in styrene monomer. As styrene polymerises it forms a continuous phase around discrete polybutadiene phases with occlusions of polystyrene. The styrene monomer is polymerised with traditional catalysts and is therefore in the atactic amorphous phase. Some of the rubber is
25 chemically grafted to the polystyrene phase. Therefore, HIPS has excellent toughness through the intimate incorporation of the polybutadiene rubber.

Another preferred impact modified styrenic polymer is super high impact polystyrene, sold by Dow Chemical Company under the trade name AIM[®]. AIM[®] is a
30 HIPS-like product with improved incorporation of the rubbery phase. Hence, AIM[®] is a very tough material and is an excellent material for preparing the sealing members of

this invention. AIM[®] differs from impact modified general purpose polystyrene, impact modified syndiotactic polystyrene and conventional high impact polystyrene in that it exhibits improved plastic deformation characteristics. Specifically, AIM[®] can undergo a yield and ductile deformation similar to nylon. This allows the material to experience higher strains than impact modified general purpose polystyrene, impact modified syndiotactic polystyrene and conventional high impact polystyrene before cracking of the sealing member and leakage of the galvanic cells can occur.

The impact modified styrenic polymer blend used to prepare the galvanic cell sealing members preferably contain the minimum amount of impact modifier which is necessary to allow the sealing member to be installed into the galvanic cell without cracking or breaking, for example when a nail is installed through the sealing member or when the battery can is crimped to seal the cell. Unmodified styrenic materials such as general purpose polystyrene and syndiotactic polystyrene would be ideal materials for sealing members for galvanic cells containing an alkaline electrolyte because of their relatively low cost, good processing characteristics, moisture independent physical characteristics, and resistance to alkaline media. However, unmodified styrenic materials are excessively brittle and must be blended with an impact modifier before being moulded into a battery seal.

20

In the case of polyolefinic elastomer impact modifiers, suitable blends comprise from 60 to 95% by weight styrenic polymer and from 5 to 40% by weight of polyolefinic elastomer based on the total weight of styrenic polymer and polyolefinic elastomer impact modifier, with blends comprising from about 80 to about 90% by weight styrenic polymer and about 10 to about 20% by weight polyolefinic elastomer being preferred. In the case of tri-block copolymer impact modifiers, the impact modified styrenic polymer blends may contain from about 50 to about 95% by weight styrenic polymer and from about 5 to about 50% by weight tri-block copolymer impact modifier based on the total weight of styrenic polymer and impact modifier, and more preferably from about 80 to about 90% styrenic polymer by weight and from about 10 to about 20% tri-block copolymer by weight. In the case of high impact polystyrene and

30

super high impact polystyrene, the styrenic polymer phase may comprise from about 60% to about 95%, and the rubbery phase may comprise from about 5% to about 40% by weight, based on the total weight of the styrenic phase and the rubbery phase.

5 We have also discovered that while sealing members prepared from the impact modified styrenic polymers described above exhibit several outstanding performance characteristics as compared with conventional nylon battery sealing members, the styrenic polymer sealing members can sometimes exhibit unacceptable leakage, especially at higher temperatures. This problem is due to the relatively high rate of stress relaxation of the styrenic polymer blends. This problem can be overcome by
10 changing the design of the sealing member to counteract the effects of stress relaxation, e.g., such as by using a resilient or springy retainer or washer which acts on the sealing member to compensate for stress relaxation. However, as another alternative which does not require design changes, the styrenic polymer blends can be modified by adding
15 an anti-stress relaxation agent.

For example, poly(phenylene oxide) (PPO) can be added to the styrenic polymer blend to reduce stress relaxation. An amount of anti-stress relaxation which is effective to achieve a desired reduction in stress relaxation can be easily determined by those
20 having ordinary skill in the art by conducting routine experiments. An example of a commercially available styrenic polymer blend exhibiting reduced stress relaxation is available from GE Plastics under the trade name Noryl®. The Noryl® products are a blend of HIPS and PPO. Noryl® EM6101 exhibits a suitable combination of properties for use as a battery seal material and will lower the overall cost of alkaline cells while
25 allowing for even lower profile sealing members than nylon. Based on standardised bench top tests, Noryl® blends have better thermal, creep and stress relaxation resistance than nylon and other conventional materials. Adding PPO to styrenic seal materials does not decrease their chemical stability in the in-cell environment.

30 Other types of anti-stress relaxing agents include inorganic fillers such as talc, calcium carbonate, carbon black, and silica.

Various tests were conducted which demonstrate that the impact modified styrenic polymeric materials have certain performance characteristics which provide improved galvanic cell sealing member performance.

5

POTASSIUM HYDROXIDE COMPATIBILITY TEST

Potassium hydroxide compatibility tests were conducted on impact modified styrenic polymer compositions and compared with similar compatibility tests on nylon.

10 The tests were conducted at high temperatures to accelerate degradation. The materials were not under stress. However, it is not expected that stress would dramatically influence the comparison.

Potassium hydroxide resistance for nylon and unmodified general polystyrene
15 were compared by floating nylon and general purpose polystyrene tensile bars (3.2 mm (1/8 inch) thick) on a 37% potassium hydroxide solution in a fluoropolymer vial placed in an oven at 130°C for 35 days. The bars were periodically removed, weighed and replaced into the solution. The results (shown in Figure 2) indicate that the unmodified general purpose polystyrene tensile bar did not have an appreciable weight loss after 35
20 days, whereas the nylon 66 tensile bar had approximately a 14% weight loss after 35 days of exposure to the 37% potassium hydroxide solution at 130°C.

Microtensile bars (0.8 mm (1/32 inch) thick) with a 0.23 mm (0.009 inch) thick section were moulded from nylon (Zytel 101F), unmodified general purpose
25 polystyrene, unmodified syndiotactic polystyrene, and impact modified syndiotactic polystyrene. Each of the microtensile bars were submerged in 37% potassium hydroxide solution in a sealed fluoropolymer bottle and placed in an oven at 95°C for 39 days. The bars were periodically removed, weighed and replaced into the solution. The results (shown in Figure 3) demonstrate that none of the styrenic polymer materials had
30 any appreciable weight loss during the testing period, whereas the nylon microtensile bar had approximately a 4.5% weight loss after 39 days of exposure to the 37%

potassium hydroxide solution at 95°C. The results shown in Figures 2 and 3 strongly suggest that the styrenic polymer based materials, whether modified or unmodified, are more resistant to degradation when exposed to potassium hydroxide than nylon.

5 To verify that the styrenic materials are not degrading when exposed to potassium hydroxide, attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy was used to evaluate any chemical changes at the surface of the specimens. Figure 4 shows that the locations of the absorbent peaks and the relative heights of the peaks are about the same for general purpose polystyrene samples which
10 have been untreated, and for those which have been exposed to a 37% potassium hydroxide solution at 130°C for 39 days. Similar results were found for unmodified syndiotactic polystyrene, impact modified general purpose polystyrene, and impact modified syndiotactic polystyrene. The results confirm that no significant potassium hydroxide degradation has occurred on the surfaces of the styrenic polymer materials.

15

In contrast, Figure 5 shows many changes in the ATR-FTIR spectrograph of untreated nylon as compared with nylon which has been exposed to a 37% potassium hydroxide solution at 130°C for 39 days. The changes in the spectrographs for the nylon samples are due to new peaks associated with degradation products of nylon. Two large
20 changes are present at the 3,000-3,500 cm^{-1} region where primary amine groups absorb, and at the 1500-1600 cm^{-1} where carboxylic acid salts absorb. The amine peaks wash out the 3,100 cm^{-1} peak and the carboxylic acid group is seen as a definite shoulder on the 1550 cm^{-1} peak. The presence of the amine end groups is consistent with the anticipated degradation products based on the hydrolysis mechanism of nylon in water.

25

Gel permeation chromatography (GPC) was used to further characterise changes on the samples exposed to potassium hydroxide solutions. To concentrate on the exposed area of the samples, shavings taken from the surface were used to measure molecular weight. The results of the GPC analysis are shown in Table 1. The
30 potassium hydroxide treatments decreased the nylon (Zytel) molecular weight by a factor of 25, and in the worst case, decreased the polystyrene molecular weight by, at

most, 15%. However, that particular condition was a 130°C test where the sample was floated on the surface of a 37% potassium hydroxide solution, and hence exposed to air. At 130°C for 39 days, it is possible that the polystyrene may experience some thermal oxidative degradation. Even so, it has a small influence on molecular weight. The results demonstrate that the styrenic polymer based materials are much more stable in potassium hydroxide than nylon. The results suggest that nylon weight loss is due to the production of very low molecular weight degradation products which can dissolve into the aqueous environment, whereas the changes in molecular weight for the styrenic polymer samples were relatively modest in comparison.

TABLE 1

Weight Average Molecular Weight (Mw in Daltons), Mean \pm S.D. n=2				
	GPPS	GPPS	GPPS-Impact Modified	Zytel 101F 80% regrind
Control (untreated)	318,000 \pm 83	303,200 \pm 2500	316,800 \pm 2500	65,700 \pm 4200
Treated in 37% KOH @ 95°C for 35 days	312,200 \pm 1600		320,200 \pm 200	2500 (n=1)
Treated in 37% KOH @ 130°C for 39 days		257,300 \pm 30		2700 \pm 300

INITIAL MOULDING TRIAL

Galvanic cell sealing members were moulded from 9 different lots of polystyrene, including tri-block modified general purpose polystyrene containing 10% and 20% tri-block impact modifier, tri-block modified syndiotactic polystyrene containing 10 and 20% tri-block impact modifier, polyolefinic impact modified general purpose polystyrene containing 10 and 20% impact modifier, polyolefinic impact modified syndiotactic polystyrene containing 10 and 20% olefinic impact modifier, and high impact polystyrene containing 7.5% butadiene rubber. The sealing members were installed in AA type batteries with minimum processing adjustments.

All of the sealing members performed favourably with some cracking upon installation of the rivets. However, it must be understood that the moulds used were designed to make nylon sealing members. The moulds have dimensions which will be different from those of moulds which are designed specifically for moulding sealing members of impact modified styrenic polymer blends. This difference is attributable to the fact that the amount of moisture absorbed by the nylon is lower during moulding than during use, which result in the nylon sealing member having different dimensions during use than immediately after moulding. In contrast, the impact modified styrenic polymer blends do not absorb significant amounts of moisture and do not experience any appreciable dimensional changes during use, as compared with immediately after moulding. It is expected that the cracking observed in some cases during installation of the impact modified styrenic polymer sealing members will be reduced or eliminated when moulds specially designed for moulding the styrenic polymer based sealing members are used.

15

OXIDATION TESTING

The HIPS and AIM[®] products both contain polybutadiene rubber. Polybutadiene rubber contains unsaturated bonds which are susceptible to oxidative attack. Oxidation of the rubber content will embrittle the material and change its performance. Alkaline galvanic sealing members were moulded from HIPS with a thin section for rupture to relieve high internal cell pressures. The pressure at which the thin section ruptures is a function of the design and the material properties of the sealing member. The data (shown in Table 2) demonstrate that the vent pressure does not change after thermal oxidative ageing. Additionally, gel permeation chromatography analysis results (shown in Table 3) demonstrate that the molecular weight of the HIPS product increases minimally after 10 weeks at 71°C. Accordingly, oxidation of HIPS and AIM[®] should not be a significant problem in this application.

TABLE 2

Material	Vent Pressure, (psi)*
HIPS	769 \pm 27
HIPS - aged 10 weeks in air at 71°C	804 \pm 50

*All data presented in this document with \pm standard deviation

5

TABLE 3

Material	Number Average Molecular Weight, Mn	Weight Average Molecular Weight, Mw	Polydispersity (Mn/Mw)
HIPS	127,000 \pm 200	227,000 \pm 1,000	1.79 \pm 0.01
HIPS - aged 10 weeks in air at 71°C	129,00 \pm 100	241,000 \pm 500	1.88 \pm 0.00

GLASS TRANSITION TEMPERATURE

- 10 The glass transition temperature of a plastic material is the temperature at which the amorphous phase of the material undergoes a transition from a glassy state to a flexible state involving motion of long segments in the polymer chain. Near and above the glass transition temperature, the material will undergo increased stress relaxation and creep. The glass transition temperature for various materials is shown in Table 4.
- 15 The data indicates that the styrenic materials have two advantages when used as a sealing member for galvanic cells having an alkaline electrolyte. First, because styrenes do not absorb water, the glass transition temperature does not depend upon moisture. Second, the glass transition temperature of the polystyrene matrix, which dominates the relaxation behaviour, is higher than polypropylene and nylon 66 at any moisture level.
- 20 High temperatures for battery end use can be as high as 85°C. Therefore, the styrenic polymer based materials undergo less stress relaxation and less creep than nylon 66.

TABLE 4

Material	Glass Transition Temperature, °C
Nylon 66 - dry as moulded	80°C ¹
Nylon 66 - 2.5% H ₂ O	40°C ¹
Nylon 66 - 8.5% H ₂ O	-15°C ¹
Talc Filled Polypropylene Homopolymer	11°C
Impact Modified SPS	100°C
Impact-Modified GPS	100°C
HIPS	100°C
AIM	100°C

LINEAR THERMAL EXPANSION

5

Thermal cycling of batteries occurs during their lifetime. Accordingly, preferred sealing member materials should undergo minimal thermal expansion, i.e., have lower co-efficiency of linear thermal expansion. The data shown in Table 5 indicates that, except for general purpose polystyrene, styrene materials have a co-efficient of linear

10

thermal expansion which is as low or lower than nylon.

TABLE 5

Material	Coefficient of liner thermal expansion x 10 ⁻⁵ (cm/cm/K) @ 25°C
Nylon 66	8.1
Talc Filled Polypropylene Homopolymer	9.8
Impact Modified SPS	6.8
Impact Modified GPPS	9.0

HIPS	6.8
AIM	8.1

DEFLECTION TEMPERATURE UNDER LOAD - ASTM D648

The heat resistance of a galvanic sealing member is crucial to maintaining a seal and preventing leakage of electrolyte. The deflection temperature under load (DTUL) is a normalised method of determining the temperature at which a material is deflected under a specified amount of load. A higher DTUL indicates that a material has better resistance properties. The data shown in Table 6 indicates that at the lowest stress, nylon 66 has the most heat resistance. However, at loads closer to those normally experienced by a sealing member in a galvanic cell, AIM[®] with low moulded-in stress and impact modified syndiotactic polystyrene show the most heat resistance. Nylon 66 has less heat resistance as it absorbs moisture. The styrenic based materials do not have this deficiency because they do not absorb water. From this analysis, styrenic based materials are expected to have better heat resistance properties, as they relate to sealing members for galvanic cells, than nylon and filled polypropylene.

TABLE 6

Material	@ 66 psi (°C)	@ 264 psi (°C)
Nylon 66 - dry as moulded	210-243 ³	65-90
Talc Filled Polypropylene Homopolymer	-	82
Impact Modified SPS	100	104
Impact Modified GPPS	-	78
HIPS	-	78-82
AIM - low moulded-in stress	96	93
AIM - high moulded-in stress	85	74

PHYSICAL PROPERTIES

A comparison of the ultimate tensile strength, ultimate elongation, and toughness (notched Izod) of various materials is set forth in Tables 7, 8 and 9, respectively. Table 7 shows that the ultimate tensile strength of the styrenic polymer based materials is less than 50% of the ultimate tensile strength of nylon 66, and about the same or lower than the ultimate tensile strength of talc filled polypropylene homopolymer. The lower ultimate tensile strength of styrenic based polymeric materials is an advantage with respect to the moulding of sealing members for galvanic cells. In particular, because of the lower ultimate tensile strength of the styrenic polymer based materials, they can be moulded with relatively thicker sections, which makes the moulding process easier.

TABLE 7

Material	Ultimate Tensile Strength (psi)	
	Dry as moulded	2.5% H ₂ O
Nylon 66	12,000	11,200
Talc Filled Polypropylene Homopolymer	5,300	
Impact Modified SPS	6,100	
Impact Modified GPPS	5,400	
HIPS	3,700	
AIM	3,200	

15

As shown in Table 8, the styrenic polymer based materials, especially the impact modified styrenic materials, and most particularly the impact modified syndiotactic polystyrene, have lower percentage elongation at break than nylon 66. The lower percentage elongation at break of the styrenic polymer based materials may be advantageously employed in the fabrication of galvanic cells. In particular, the amount of internal volume of the galvanic cell which is needed to allow expansion and rupture

20

of the sealing member in the event of excessive internal pressure can be significantly reduced. A reduction in the amount of space need for expansion and rupture of the sealing member in the event of excessive pressure within the galvanic cell can be advantageously utilised for other purposes, such as to design cells having improved service life or discharge capacity.

TABLE 8

Material	% Elongation at Break	
	dry as moulded	2.5% H ₂ O
Nylon	52	≥300
Impact Modified SPS	4	
Impact Modified GPPS	25	
HIPS	35	
AIM	50	

The result shown in Table 9 demonstrates that the styrenic based polymer materials are generally as tough or tougher than nylon 66. This increased toughness decreases leakage due to cracking or breakage of the sealing member during installation of the sealing member into a galvanic cell.

TABLE 9

Material	(ft lb/in)	
	dry as moulded	2.5% H ₂ O
Nylon 66	1.0	2.1
Impact Modified SPS	1.0	
Impact Modified GPPS	4.8	
HIPS	2.5	
AIM	5.5	

SURFACE ENERGY

Leakage of aqueous galvanic cells can occur when aqueous solution travels between the plastic and metal interface in the compressive sealing zone. A lower surface energy plastic will inhibit this migration compared to a high surface energy plastic. The data shown in Tables 10 and 11 indicates that styrenic polymer based materials have lower surface energy and higher water contact angles than nylon 66. Accordingly, sealing members made of the styrenic polymer based materials will have inherently better leakage performance than nylon sealing members.

TABLE 10

Material	Critical Surface Tension of Wetting (dynes/cm)
Nylon 66	46
Polystyrene	33
Impact Modifiers	near 30

TABLE 11

Material	Water Contact Angle (°)
Nylon 66	45-50*
all styrene based materials	90-100

*Decreases with increased moisture content of nylon material and with time in contact with surface.

MOISTURE ABSORPTION

Absorption of moisture has three negative effects: (1) the material requires drying before moulding, (2) the moulded part will change dimensions as a function of moisture content and hence relative humidity, and (3) the properties of the moulded part will change as a function of moisture content, and hence relative humidity. As shown in

Table 12, the styrenic polymer based materials do not absorb an appreciable amount of water and therefore do not have these unwanted side effects.

TABLE 12

Material	Equilibrium moisture (%) content in 50% RH	Equilibrium moisture (%) content in 100% RH
Nylon 66	2.5	8.5
Polysulphone	-	0.85
Impact Modified SPS	<0.1	<0.1
Impact Modified GPPS	<0.1	<0.1
HIPS	<0.1	<0.1
AIM	<0.1	<0.1

HYDROGEN PERMEABILITY

Hydrogen gas is produced in many galvanic cells. Internal pressures of galvanic cells can become dangerously high. Accordingly, a seal material that allows the permeation of hydrogen will increase the safety of the cell. As shown in Table 13, the styrenic polymer based materials have a significantly higher hydrogen permeability than conventional galvanic cell seal materials (such as nylon 66, polypropylene and polysulphone).

TABLE 13

Material	cc•mil/100in ² •day•atm
Nylon 66	33
Talc Filled Polypropylene Homopolymer	480
Polysulphone	1800
all styrene based materials	3000

INJECTION MOULDING

As illustrated in Table 14, amorphous styrene tend to cool much quicker than polypropylene or nylon 66. The cooling times set forth in Table 14 are an indication of the amount of time after injection moulding which is required for cooling and solidification of the moulded part before it can be removed from the mould. Shorter cooling times result in shorter moulding cycle times and higher production rates for a given moulding apparatus.

TABLE 14

wall thickness (mm)	Cooling Time (seconds) ⁴		
	Amorphous Styrenes	Polypropylene	Nylon 66
0.5	1.0	1.8	-
1.0	2.9	4.5	3.8
1.5	5.7	8.0	7.0

Because the styrenic polymer based materials do not absorb appreciable amounts of moisture, drying of the styrenic polymer based materials is not required before moulding. All nylons require strict control of the resin moisture between 0.10% and 0.25% by weight. Below 0.10% by weight solid state polymerisation can occur in nylon, increasing the viscosity of the melt and making it difficult to fill the mould. Above 0.25% moulded-in bubbles and flash occur.

INITIAL SEAL PERFORMANCE

As stated above, the styrenic polymer based materials have lower tensile strengths than nylon. A manifestation of this lower tensile strength is lower than pressures for seals having a given thickness in the area which is designed to rupture, or

styrenic based polymer seals which are thicker in the area which is designed to rupture at a given pressure. Identically configured seals made of various materials were tested to determine the pressure at which the vent area of the seal would rupture. These results are set forth in Table 15. Because of the lower tensile strength of the styrenic polymer based materials, the rupture areas of the seals can be made thicker. This allows easier injection moulding of the seals.

TABLE 15

Material	Vent Pressure, (psi)
Nylon 66	near 1200
SPS + 10% Styrenic Impact Modifier	752 \pm 102
SPS + 20% Styrenic Impact Modifier	567 \pm 99
SPS + 10% Olefinic Impact Modifier	457 \pm 91
GPPS + 10% Styrenic Impact Modifier	994 \pm 48
HIPS	769 \pm 27

10 SUMMARY OF EXPERIMENTAL RESULTS

The data set forth above demonstrates that the impact modified styrenic polymer blends have highly advantageous properties for use in forming a sealing member for a galvanic cell, especially sealing members for cells having an alkaline electrolyte. The data show that polyamides (such as nylon) are susceptible to chemical attack by the chemical environment of the battery. Polyamides also absorb moisture from the environment that change their dimensions and mechanical properties. Polypropylenes (mineral filled and un-filled) undergo extensive softening at temperatures experienced by the battery (e.g., 70-80°C) which can cause leakage and unreliable performance. Polysulphone is costly, requires extremely high temperatures and low moisture levels to properly manufacture the seal via injection moulding.

Polystyrenes of various tacticities and levels of impact modification (through compounding with elastomers) are not susceptible to chemical attacks by the chemistry of an alkaline galvanic cell, do not absorb appreciable moisture, do not soften until temperatures above which polypropylene (mineral filled and un-filled) will soften and are easily fabricated via injection moulding, as they do not require drying and can be processed at much lower temperatures than polysulphone.

For use of a galvanic cell sealing member, polystyrene requires toughening by blending with elastomeric polymers (impact modification agents). However, too much impact modification is not desirable, but will instead lead to softening of the polystyrene at high temperature (70-80°C). Experimentation has shown that polyolefin or hydrogenated rubber/styrene are two types of elastomers that are acceptable for use in impact modification. However, any rubbery polymeric material may function in this application.

Atactic or syndiotactic polystyrene are acceptable for use in alkaline galvanic cells. Syndiotactic polystyrene form crystalline microstructure while the atactic polystyrene is amorphous. Both atactic and syndiotactic polystyrene have a glass transition temperature of 100°C. Near and above this temperature, syndiotactic polystyrene is preferred because the crystalline structure will maintain the mechanical strength of the materials while the atactic polystyrene will soften due to the absence of the crystallites, which do not melt until 270°C. Hence, in applications near or above 100°C syndiotactic polystyrene is highly preferred.

EXPERIMENTAL:

Cell Trial

AA factory product seals were moulded from Noryl® EM6101. These seals were moulded with a mould temperature 200°F and a melt temperature of 560°F. Two hundred seals were assembled into collectors and then assembled into AA cells.

Chemical Stability of Noryl®

One-eighth inch thick plaques of Noryl® EM6101 were moulded. Sections of these were placed in 37% KOH or a EMD slurry with KOH at 71°C for 16 weeks. These samples were then analysed for chemical degradation by measuring their molecular weight via gel permeation chromatography (GPC). If any degradation was to occur, it would be concentrated at the surface where the Noryl® was in contact with the corrosive environment. Therefore, the upper 10µm of the samples' surfaces were collected by slicing it off with a microtome. It was this 10µm thick shaving that was dissolved for GPC analysis.

--- GPC analysis was performed. Molecular weight statistics were calculated using the following definitions.

$$\text{Number Average Molecular Weight, } M_n = \sum N_i M_i / \sum N_i$$

$$\text{Weight Average Molecular Weight, } M_w = \sum N_i M_i^2 / \sum N_i M_i$$

Wherein N_i is the number of polymer chains of molecular weight M_i

The number average molecular weight is simply the mean weight of all the polymer chains in the sample. The weight average molecular weight is the second moment of the distribution where the chains with higher weight count more toward its value. If the polymer chains in a sample are all equal in length then the number average and weight average are equal (the polydispersity (M_w/M_n) is unity).

RESULTS AND DISCUSSION:**Chemical Compatibility of Noryl**

Table 16 shows the GPC results from accelerated ageing of Noryl® EM6101. The data reveals that the molecular weight of the surface of Noryl® EM6101 does not change with treatment in the harsh KOH and EMD environments. As shown previously, HIPS is much more stable to these harsh environments than Zytel® 101F.

Figure 1 shows that adding PPO to HIPS does not decrease the stability of HIPS since no hydrolytic or oxidative chain scission occurred during the treatment of the Noryl.

TABLE 16

	CONTROL	71°C KOH	71°C MnO ₂
Mn	8,000	9,000	8,000
Mw	36,000	35,000	32,000
PDI 5000	22,000	19,000	18,000

5 Improved Thermal and Creep Properties

Table 17 shows the heat deflection temperatures (HDT) of Zytel® 101F, and Noryl® EM6101. Heat deflection temperatures are obtained by placing a fixed load on a test specimen and the heat of the specimen is increased until the specimen softens enough to deflect a given distance. Therefore, HDT measures the creep of a material as temperature increases. The higher the HDT, the more resistance the material is to heat and creep. The data clearly show that Noryl® EM6101 is the most resistant material to heat and creep. The increased resistance is due to the PPO in the Noryl.

TABLE 17

MATERIAL	HEAT DEFLECTION TEMPERATURE
Nylon 66-dry	90
HIPS	78
Impact Modified SPS	80
Noryl® EM6101	121

15 Improved Stress Relaxation Properties

The reason for poor leakage performance for styrenic seal materials was their inherently high rate of stress relaxation. The increased HDT of Noryl's would suggest

that the rate of stress relaxation of these materials should also be decreased, lending to improved leakage performance. Figure 6 below displays the stress relaxation of Zytel® 101F, HIPS, and Noryl® 6100. Figure 7 graphically displays the rate of stress relaxation. These graphs show that the stress in Noryl decays out at the lowest rate.

- 5 Therefore, it is expected to maintain the compressive stress in the sealing zone of an alkaline sealing member the longest and hence give the best leakage resistance.

It is understood that the embodiments shown in the drawings and described above are merely for illustrative purposes and not intended to limit the scope of the

- 10 invention.

CLAIMS:

1. A galvanic cell sealing member formed of a high impact styrenic polymer blend.
- 5 2. A sealing member according to claim 1, wherein the styrenic polymer blend comprises a blend a styrenic polymer and an impact modifying agent.
3. A sealing member according to claim 2, wherein the styrenic polymer blend comprises from about 50 to about 95% by weight of a styrenic polymer and from about
10 5 to about 50% by weight of an impact modifying agent which increases the toughness of the styrenic polymer, based on the total weight of the styrenic polymer and the impact modifying agent.
4. A sealing member according to any preceding claim, wherein the styrenic
15 polymer blend comprises atactic polystyrene, syndiotactic polystyrene, or both.
5. A sealing member according to any preceding claim, wherein the styrenic polymer is syndiotactic polystyrene.
- 20 6. A sealing member according to any of claims 2 to 5, wherein the impact modifying agent is a polyolefinic thermoplastic elastomer.
7. A sealing member according to claim 6, wherein the styrenic polymer blend comprises from about 60 to about 95% by weight of the styrenic polymer and from
25 about 5 to about 40% by weight of the impact modifying agent, based on the total weight of the styrenic polymer and the impact modifying agent.
8. A sealing member according to any of claims 2 to 5, wherein the impact modifying agent is a tri-block copolymer.

9. A sealing member according to claim 8, wherein the tri-block copolymer is selected from styrene-butadiene-styrene, styrene-isoprene-styrene, styrene-ethylene/butylene-styrene, and styrene-ethylene/propylene-styrene.

5 10. A sealing member according to any of claims 2 to 9, wherein the styrenic polymer blend comprises from about 70% to about 95% of the styrenic polymer and from about 5% to about 30% of the impact modifying agent, preferably about 80 to about 90% by weight of the styrenic polymer and from about 10 to about 20% by weight of the impact modifying agent, based on the total weight of the styrenic polymer and the
10 impact modifying agent.

11. A sealing member according to any of claims 1 to 5, wherein the styrenic polymer blend is formed of a blend of high impact polystyrene and polybutadiene rubber, and comprises a styrenic phase and discrete rubbery phase.

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12. A sealing member according to claim 11, wherein the styrenic phase comprises from about 60 to about 95% by weight and the rubbery phase comprises from about 5 to about 40% by weight, based on the total weight of the styrenic phase and the rubbery phase.

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13. A sealing member according to any preceding claim, wherein the styrenic polymer blend includes an anti-stress relaxation agent.

14. A sealing member according to claim 13, wherein the anti-stress relaxation
25 agent is poly(phenylene oxide).

15. A sealing member according to claim 13, wherein the anti-stress relaxation agent is an inorganic filler, preferably selected from talc, calcium carbonate, carbon black, and silica.

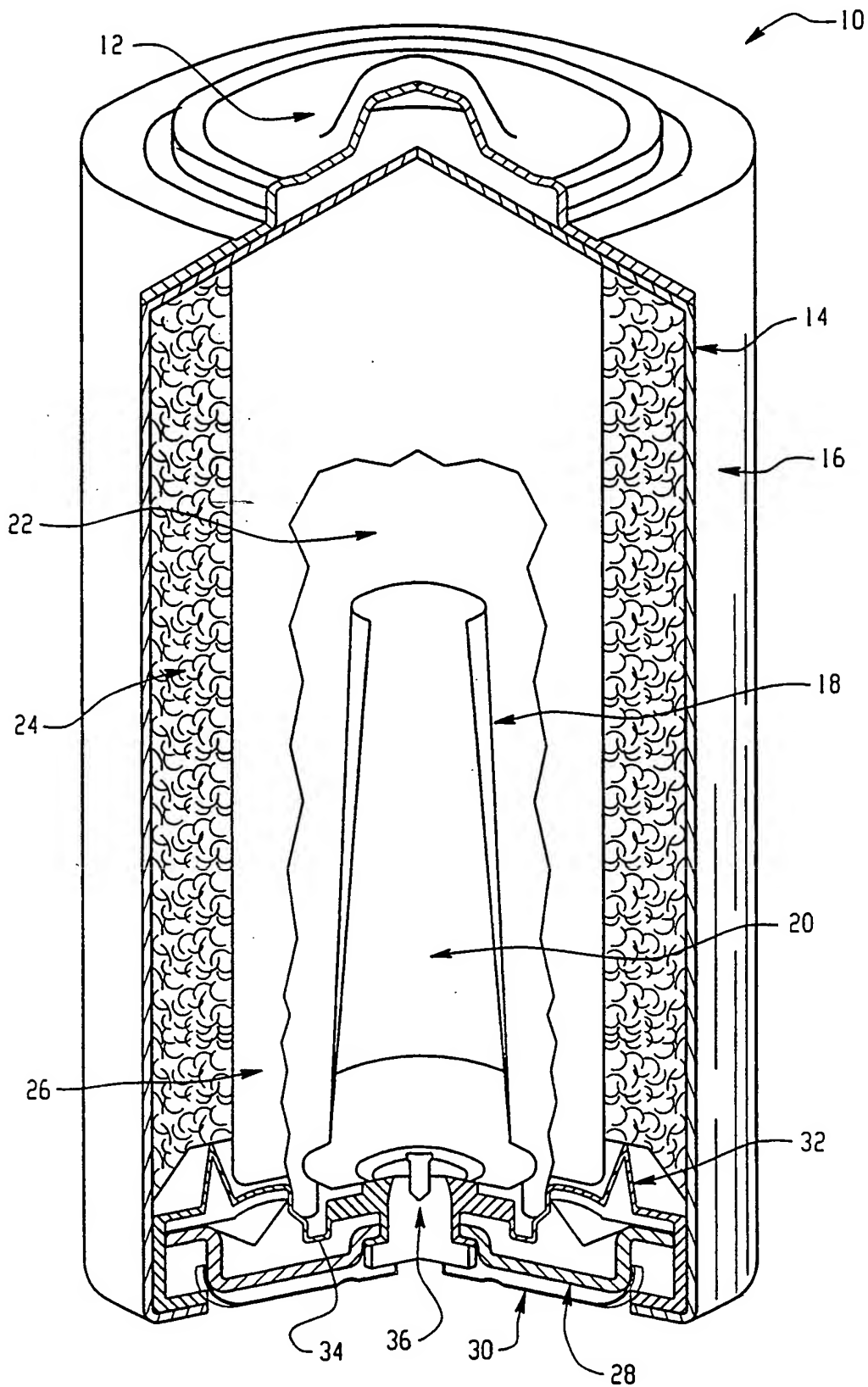
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16. A sealing member according to any preceding claim configured as a gasket for use in a miniature cell.

17. A galvanic cell including a sealing member as defined in any preceding claim.

5

18. A cell according to claim 17, wherein the cell is a miniature alkaline air cell and the sealing member is a gasket for the miniature alkaline air cell.

*Fig. 1*

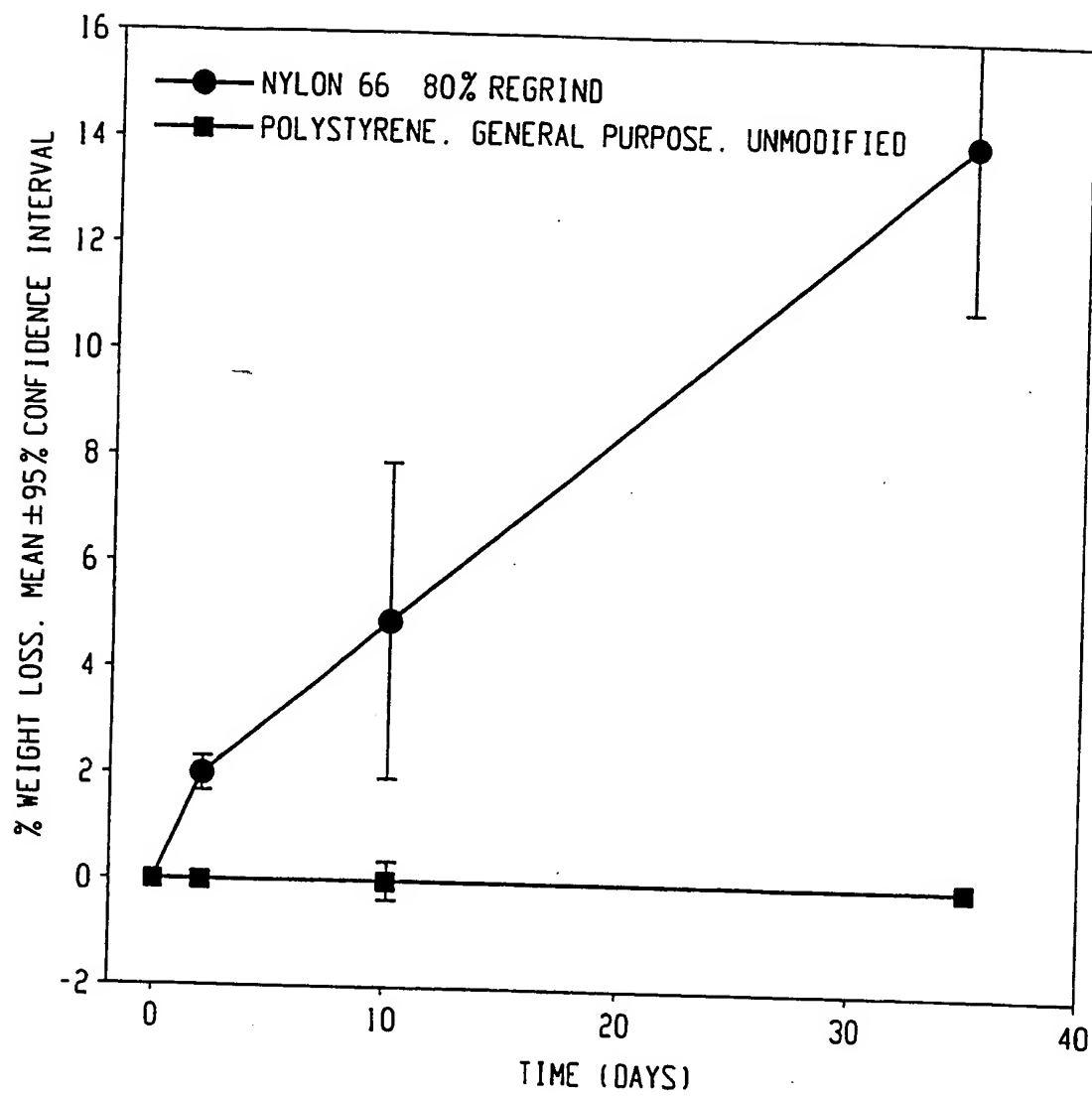
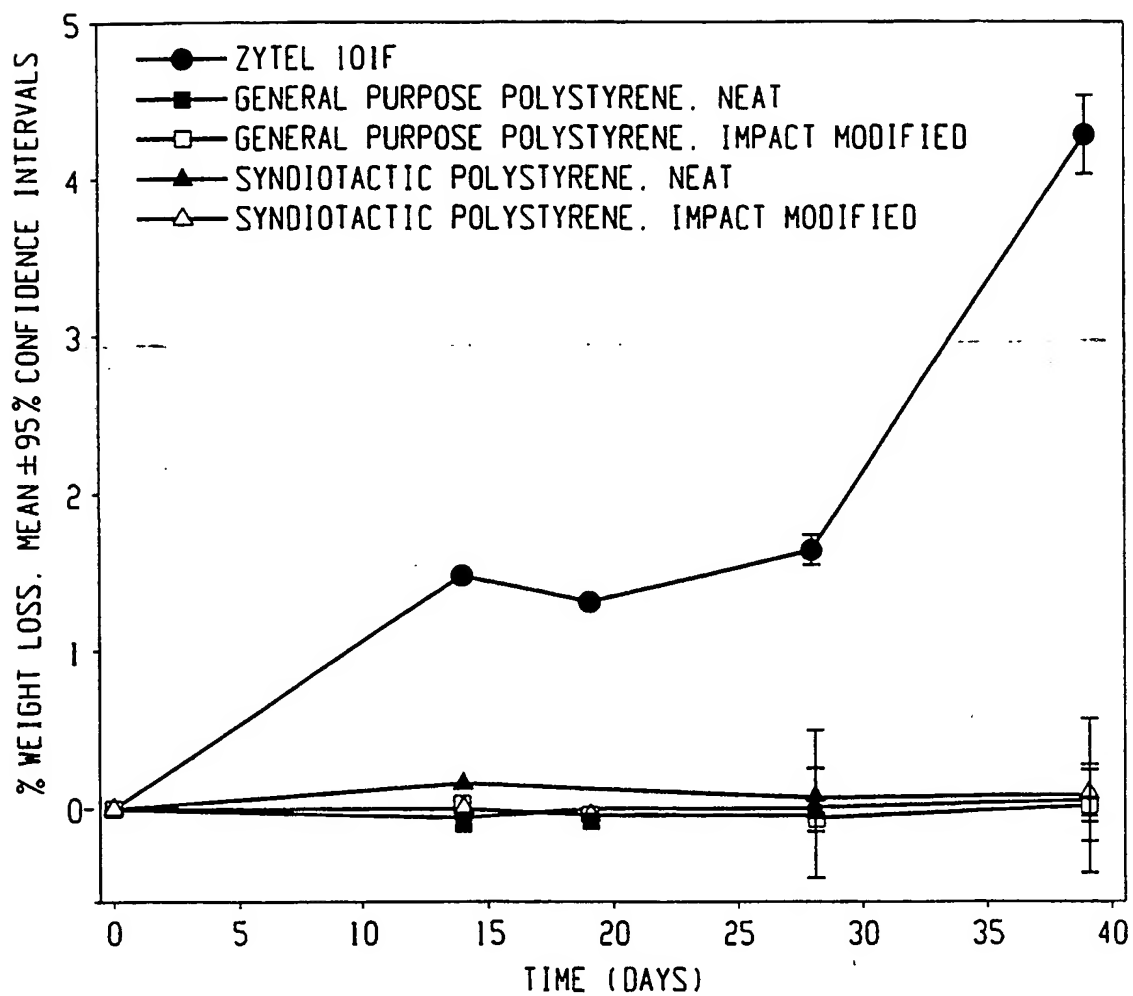


Fig. 2

*Fig. 3*

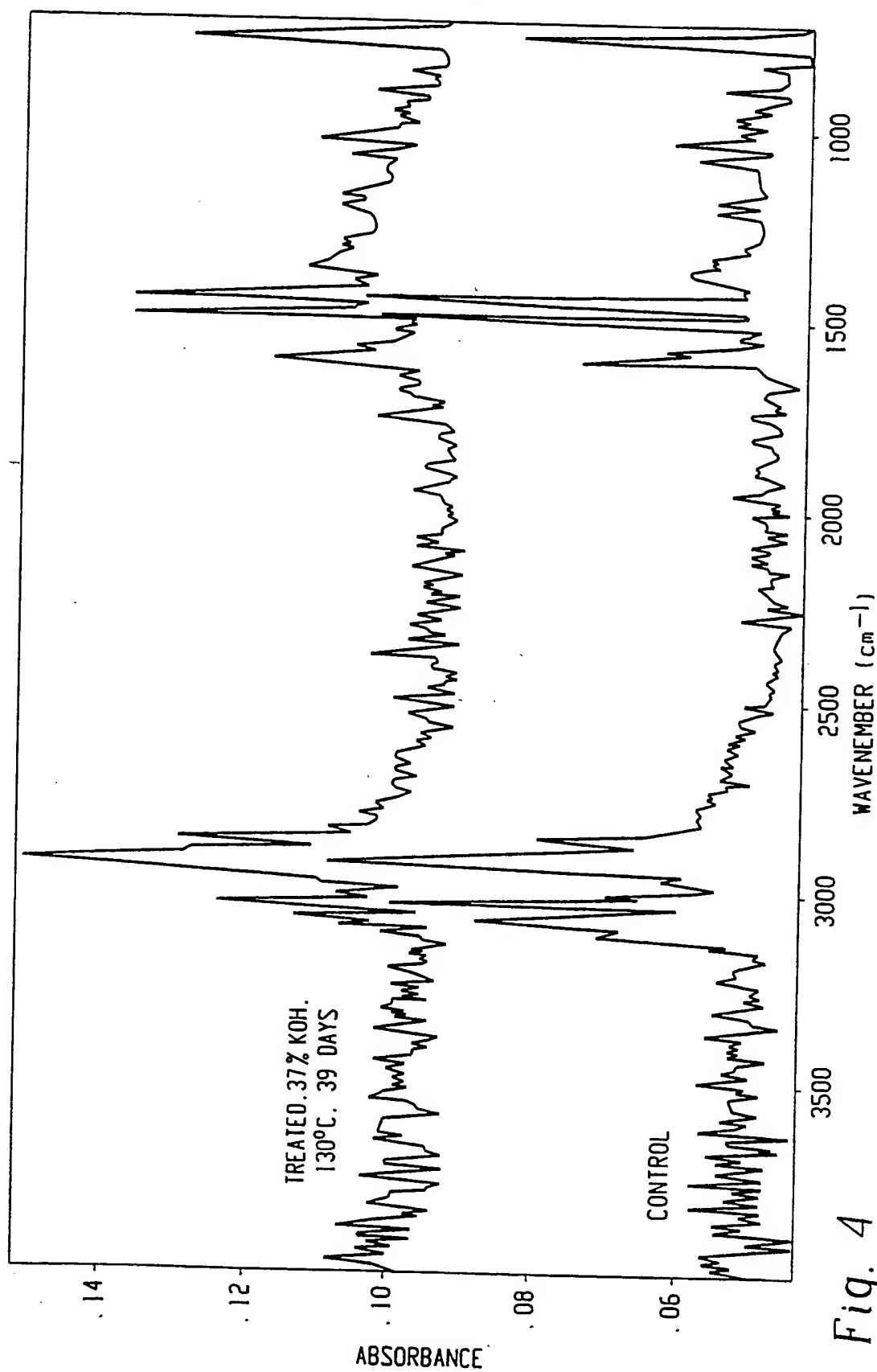


Fig. 4

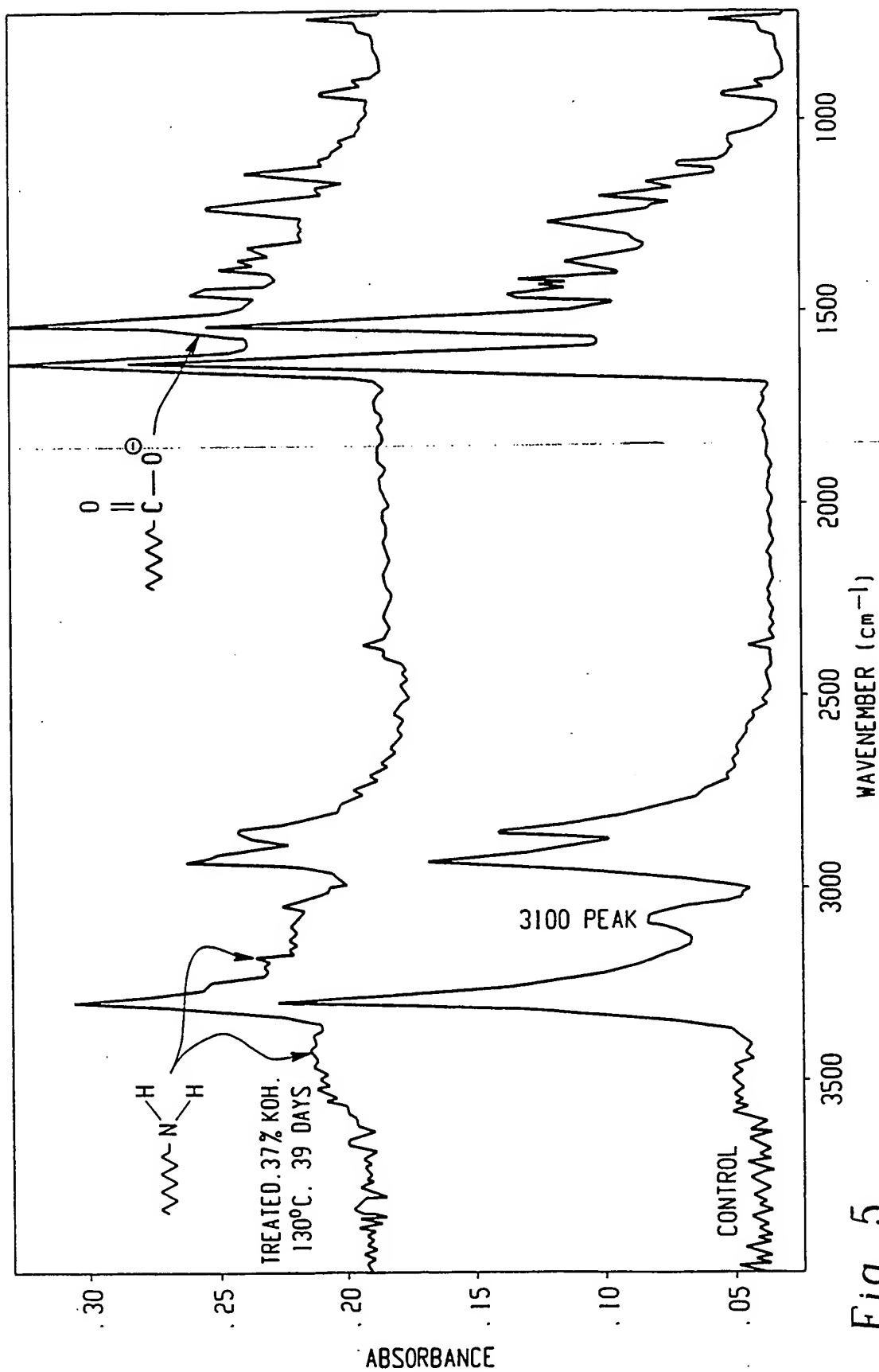
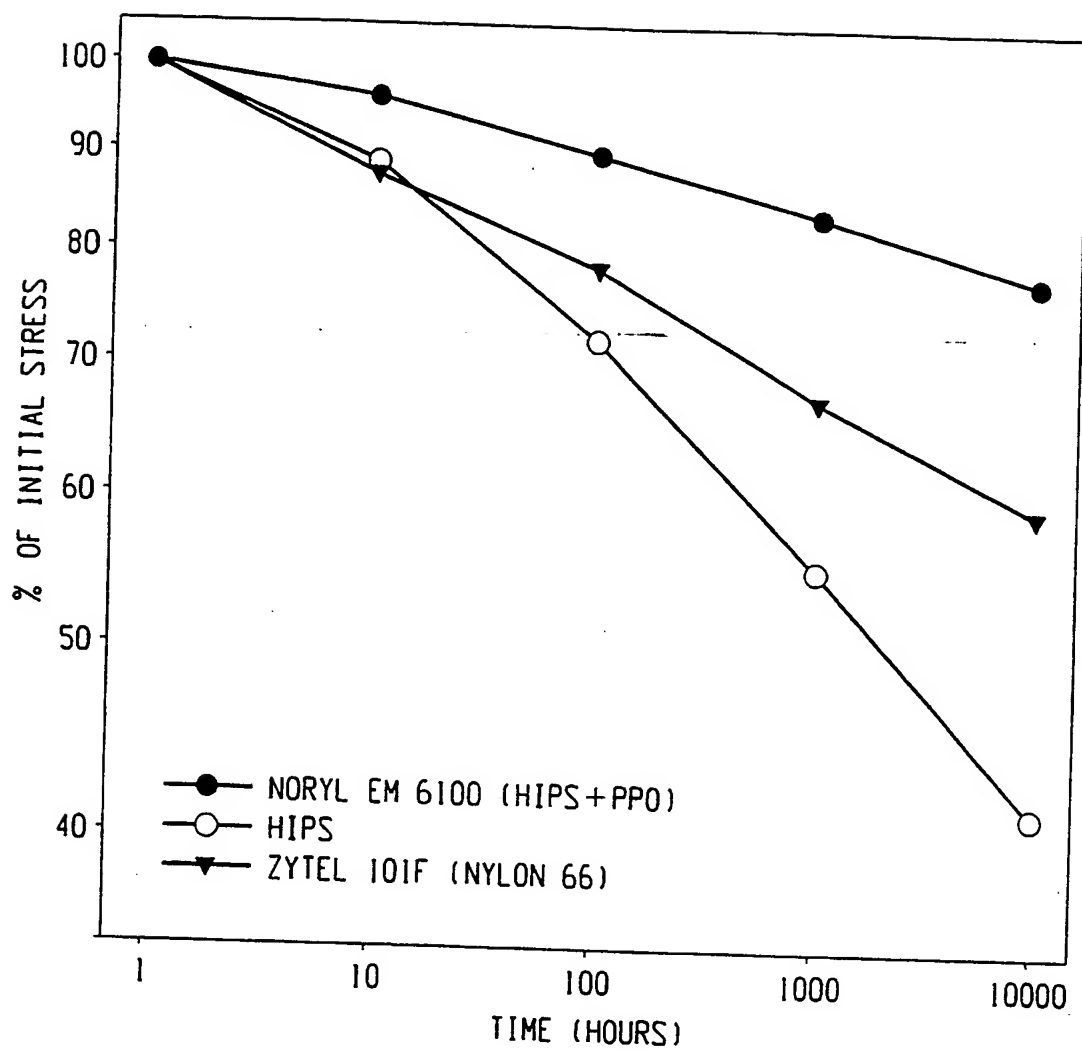
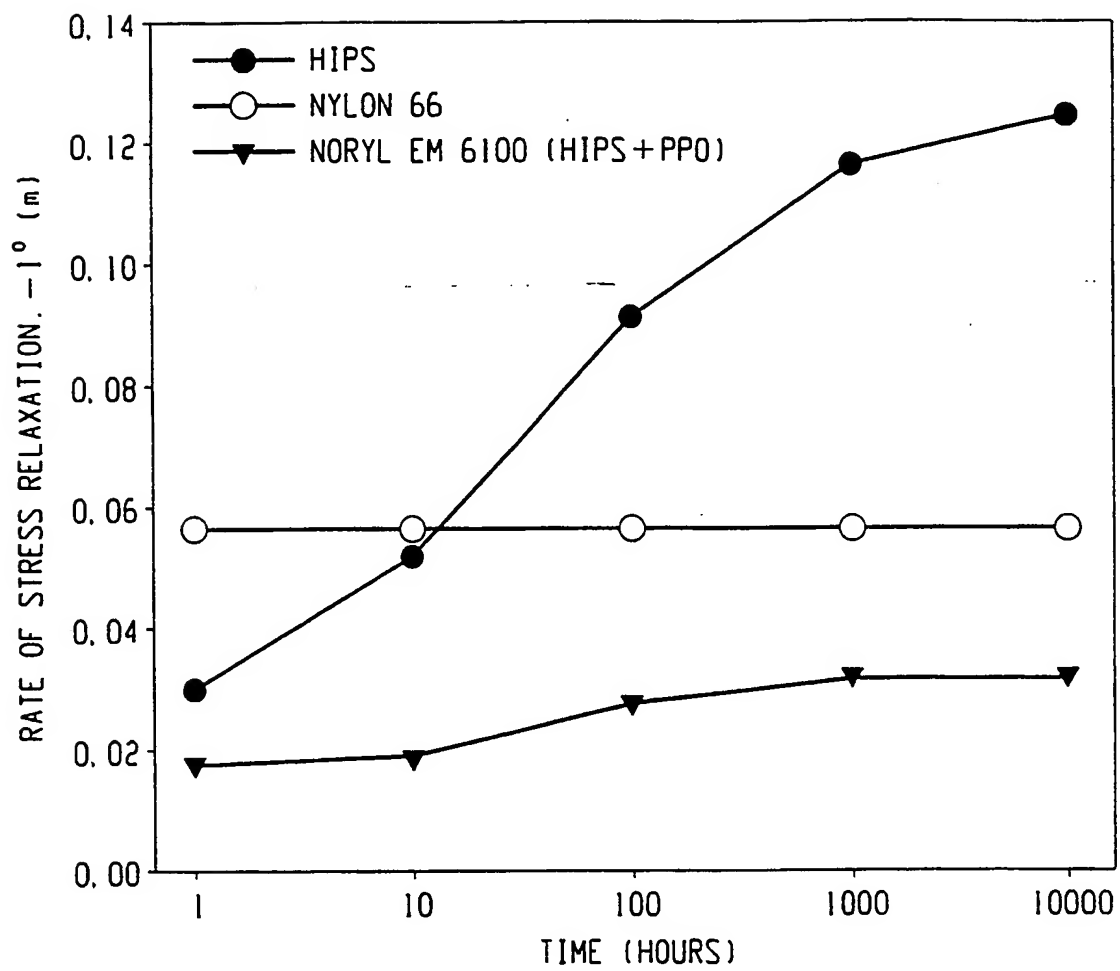


Fig. 5

*Fig. 6*

*Fig. 7*

INTERNATIONAL SEARCH REPORT

In tional Application No

PCT/US 99/30522

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01M2/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.

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INTERNATIONAL SEARCH REPORT

International Application No

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